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Deactivation by H2S of Cr2O3 Emission Control Catalyst for Chlorinated VOC Destruction

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16. ABSTRACT The paper discusses one aspect of catalyst stability (i.e., deactivation by poisoning) and the concomitant effects on catalyst activity and selectivity in the destruction of chlorinated hydrocarbons. The study was initiated because nothing is documented of the effect of H2S or the other sulfurous poisons on the performance of catalysts in the specific application of oxidative destruction of chlorinated volatile organic compounds (VOCs). A chromia (Cr2O3) catalyst, commercially popular for the destruction of chlorinated hydrocarbons, was chosen for the study of H2S poisoning effects, which concentrated on the activity, selectivity, and stability trends of the catalyst to H2S. Study results indicate that poisoning of the catalyst by H2S brings about mixed effects. While activities generally decreased, the selectivities to HCl and chloroform became more favorable and the selectivity to CO2 decreased.

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Deactivation by H_2S of Cr_2O_3 Emission Control Catalyst for Chlorinated VOC Destruction

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INTRODUCTION

Background

Chlorinated organic compounds such as methylene chloride, trichloroethylene, and carbon tetrachloride have found widespread use as solvents and degreasing agents. However, it is now known that they possess carcinogenic effects, and this has led to strict controls on their use and even stricter restrictions on their disposal.

Careless disposal of these chlorinated volatile organic compounds (VOCs) in the past has resulted in the contamination of soil and eventually groundwater. The remediation of these polluted sites and groundwater now occupies a high priority in EPA's Superfund activities.

The strategy for the decontamination of groundwater has been to carry out counter-current air stripping of the groundwater in order to transfer the chlorinated VOCs to the air stream and thereafter address the issue as an air pollution problem. While thermal incineration and, to a lesser extent, activated carbon adsorption processes are popular, destruction of these hazardous air pollutants (HAPs) by catalytic incineration is rapidly becoming an attractive alternative.

Research efforts to scientifically design superior catalyst systems for destruction of chlorinated VOCs and to understand the complex catalytic reaction mechanisms are in progress at the University of Akron. The primary requirements for a superior catalyst are threefold: (1) good activity to facilitate catalytic destruction at low temperatures, (2) high selectivity to total or deep oxidation products (HCl and CO_2) with insignificant formation of more toxic higher chlorinated species, and (3) stability in the reaction environment.

Objectives

The present study is focussed on one aspect of catalyst stability, namely deactivation by poisoning, and the concomitant effects on catalyst activity and selectivity in the destruction of chlorinated hydrocarbons.

Parametric evaluation of catalytic destruction of different HAPs performed elsewhere[1] has shown that chlorinated VOCs are especially difficult to destroy catalytically. One of the factors which contributed to the difficulty was the poisoning and deactivation of traditional oxidation catalysts, such as metals and metal oxides, by the chlorine and HCl formed during the destruction process.

The other potential poisons in the catalytic destruction of chlorinated compounds in groundwater stripper emissions are sulfurous compounds like H_2S that may be present in the groundwater and that may be transferred to the air stream. Sulfur poisoning of metal and metal oxide catalysts has been exhaustively studied[2,3] and a wealth of information exists on the effects of these poisons on the catalyst structure and morphology. However, nothing is documented of the effect of H_2S or the other sulfurous poisons on the performance of catalysts in the specific application of oxidative destruction of chlorinated VOCs. This has been the motivation for

undertaking this study.

Chromia (Cr_2O_3) catalysts are commercially popular for the destruction of chlorinated hydrocarbons. These catalysts have been chosen for the study of H_2S poisoning effects. The objective of this study was to examine the activity, selectivity, and stability trends of the catalyst to H_2S. Correlation of these trends to structural and morphological changes of the catalyst, and modeling of the catalyst deactivation by H_2S are scheduled to be studied.

EXPERIMENTAL

The H_2S exposure studies were carried out with a Cr_2O_3 catalyst supported on a low surface area (≈0.45 m^2/g) silica monolith (0.6 cm id x 1.6 cm od x 22.9 cm long, weighing approximately 60 g and obtained from Norton Co., Akron, Ohio). The Cr_2O_3 catalyst was prepared by the method of incipient wetness using an aqueous solution of chromic acid (CrO_3) as a precursor.

Methylene chloride was used as the test chlorinated VOC because of the simple product spectrum resulting from its oxidation. About 2000 ppm by volume of methylene chloride in dry air was passed through the monolith at a flowrate which gave a reactor residence time of 0.31 sec. A tubular quartz reactor with a preheated section and a catalytic reactor section was used. A schematic of the reactor and details of reactor operating conditions are given in Figure 1 and Table 1, respectively.

Reactor inlet and outlet vapors were periodically sampled and analyzed using a Hewlett Packard Model 5890 Gas Chromatograph with Model 5970B Mass Selectivity Detector to identify and quantify products. Product HCl was monitored by aqueous trapping followed by pH measurement using a Corning Ion Analyzer. Product CO and Cl_2 were detected and analyzed using MSA Draeger detector tubes. Further details of the experimental setup can be found in References 4 and 5.

The catalyst performance was studied at 500, 450, and 400 °C both before and after exposure to H_2S. At each of these temperatures, one of the runs involved the addition of about 24,000 ppm water as co-feed to the reactor. This was done to simulate the humid air environment of the catalytic incinerator unit downstream of the groundwater stripper and also to create conditions favorable to the formation of HCl rather than Cl_2 by the reversible reaction:

$$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$$

After preliminary characterization at 500, 450, and 400 °C, the monolith was exposed to a flowing stream of 5000 ppm H_2S in dry air at 500 °C for 9 hours. Once again, the flowrate was maintained to ensure a residence time of 0.31 sec. After this exposure to H_2S, the monolith was again tested at 500, 450, and 400 °C.

The results of these experiments are summarized in Table 2. Detailed chlorine and carbon balances are presented in Tables 3 and 4, respectively, while Table 5 details selectivity trends.

The selectivities to chloroform, HCl, and Cl_2 are defined as the ratios of the moles of chlorine in these products to the moles of chlorine reacted. Selectivities to CO and CO_2 are defined as the ratios of moles of carbon in these products to the moles of carbon reacted.

DISCUSSION

The conversion levels of methylene chloride, which may be used as a measure of the catalyst activity, are presented in Table 2 and the trends before and after H_2S poisoning are shown in Figure 2. It can be seen that the activity of the catalyst at the different temperatures is lower after exposure to H_2S. Thus the conversions at 500 °C before and after H_2S poisoning are around 50 and 45 percent, respectively, when water is not added to the feed stream while at 450 °C, the corresponding values are 35 and 17-22 percent, respectively. There is some scatter in data obtained at 400 °C.

Previous work[6] indicates that the catalytic activity in the destruction of methylene chloride is well correlated to the oxygen adsorption capacity of the catalyst. While it is known that the oxygen pickup by the catalyst decreases with decreasing temperature between 500 and 400 °C, the change in oxygen pickup with H_2S poisoning is yet to be verified. Such a change could occur with strong adsorption of H_2S on some of the catalyst surface sites active in the pickup of oxygen. Another possibility is the change in the nature of the surface by the formation of some form of surface sulfate.

More interesting, however, are the trends in selectivities to the various products as shown in Figures 3 through 7. Chloroform, though an undesirable product, is formed in small amounts during the destruction reaction. This could be caused by a complex interaction between methylene chloride and the chlorine formed during the oxidation reaction. The selectivity for the formation of chloroform was reduced after the catalyst had been exposed to H_2S. Conversely, it can also be seen that the catalyst becomes less selective to Cl_2 formation and that the formation of HCl is more favored after poisoning by H_2S. This would also support the belief that chloroform formation is related to the ability of the catalyst to favor the formation of Cl_2 to HCl.

Yet another interesting selectivity trend is the relative ratio of CO_2 to CO in the reaction products. While the ratio of CO_2 to CO is greater than unity prior to H_2S poisoning, CO generation was preferred to CO_2 after the catalyst had been exposed to H_2S. This preference for CO formation also appears to be a contributory factor in the generation of phosgene at 500 °C when the catalyst has been poisoned. The selectivity to CO also increases as the temperature of the reaction is lowered. This trend of increased selectivity to CO after H_2S poisoning and a further increase at lower temperatures also probably ties in with the earlier supposition that the oxygen pickup capability of the catalyst is lowered by H_2S poisoning. It is now believed that CO_2 formation in the course of methylene chloride destruction occurs in a stepwise reaction sequence via the initial formation of CO. It is possible that the reduced oxygen pickup after poisoning, especially at lower reaction temperatures, makes the formation of CO_2 from CO less feasible.

CONCLUSIONS

The above observations indicate that the poisoning of the catalyst by H_2S brings about mixed effects. While the activities generally decreased, the selectivities to HCl and chloroform became more favorable and the selectivity to CO_2 decreased. This study has been limited to examining the effects of H_2S poisoning on activity and selectivity of the catalyst. To be more useful, this information will have to be correlated to the characteristics of the catalyst that control its performance. This may be the subject of further study. It may also be valuable to test the effects of H_2S on the catalyst when it is present in the feed stream to the reactor rather than the present case wherein the catalyst had been poisoned by H_2S in isolation.

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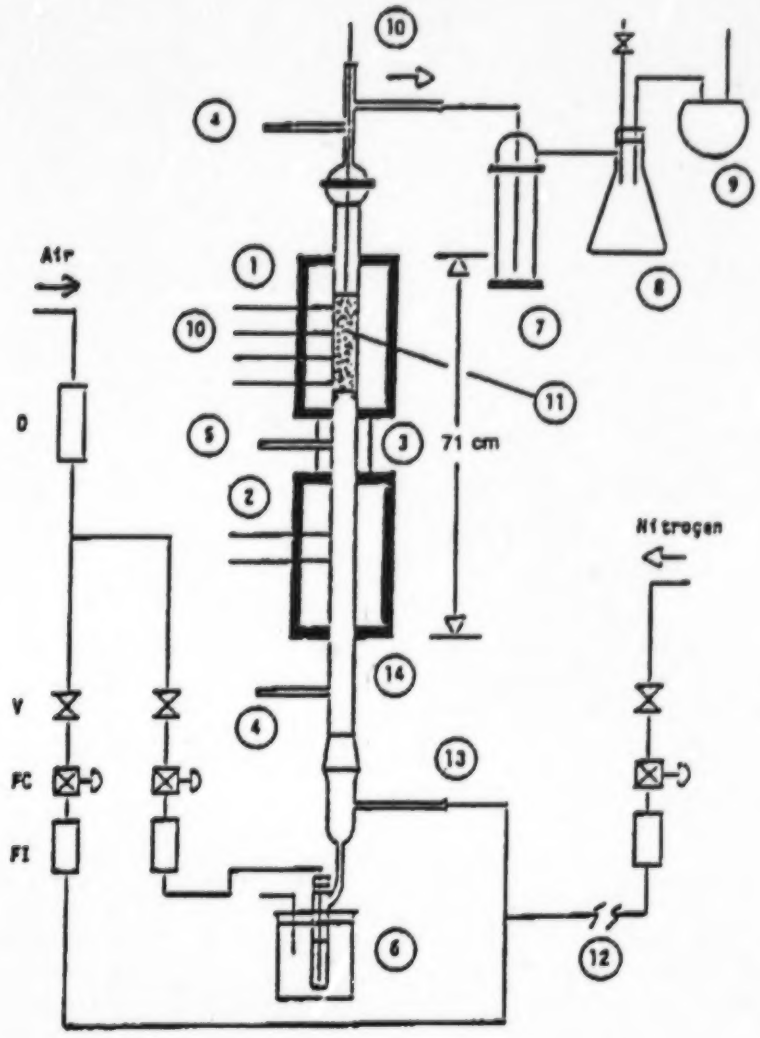

1. Reactor section
2. Preheater section
3. Heat tape and insulation
4. Sample port
5. Manometer tap
6. Chlorinated VOC bubbler
7. HCl trap
8. Surge tank
9. Vacuum pump
10. Thermocouple
11. Supported catalyst
12. Nitrogen source
13. Main air flow inlet
14. 28 mm Pyrex tube

V: Valve
FC: Flow controller
FI: Flow indicator
D: Drier

Figure 1: Catalytic reactor diagram

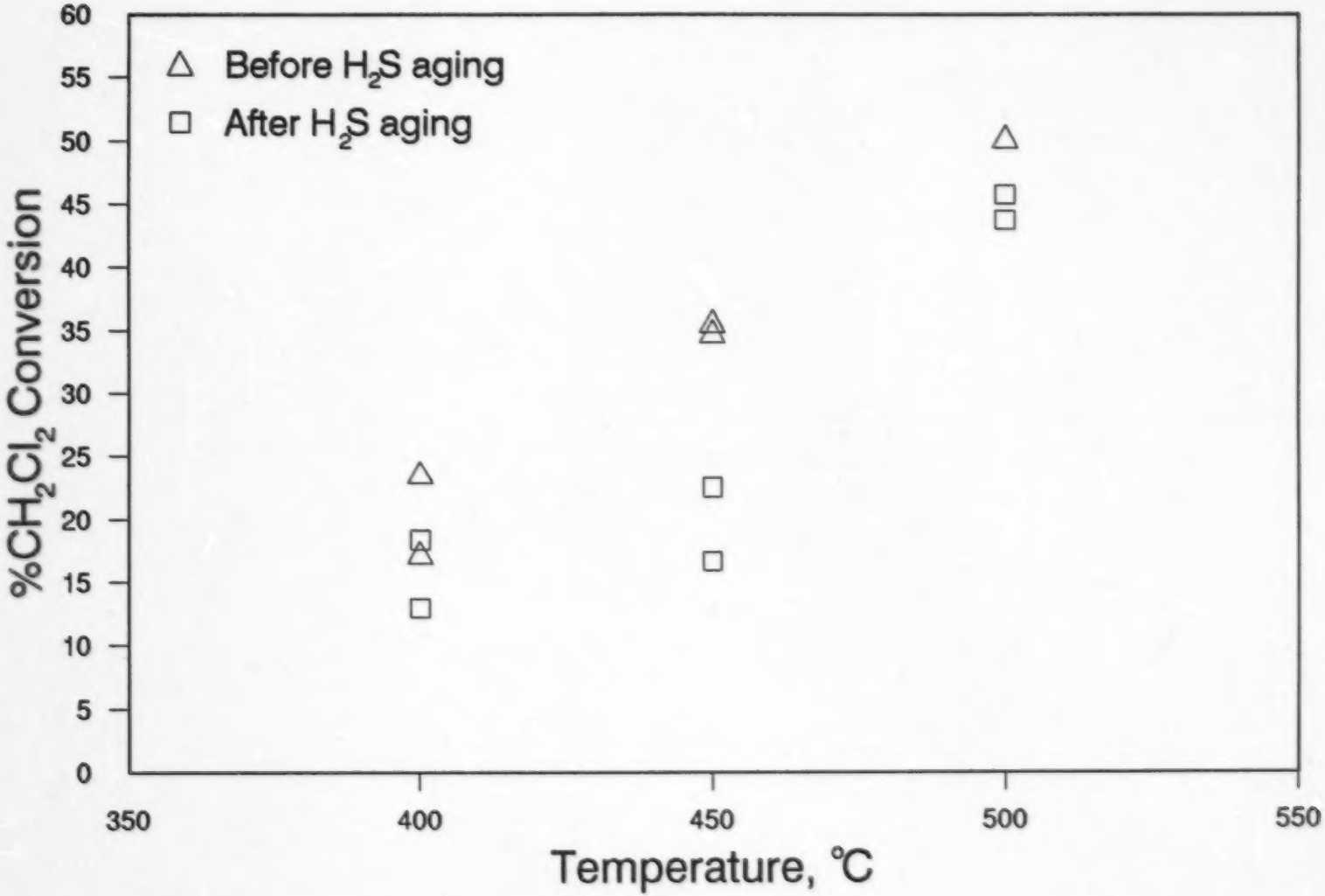

Figure 2: % Reactant conversions before and after H_2S poisoning

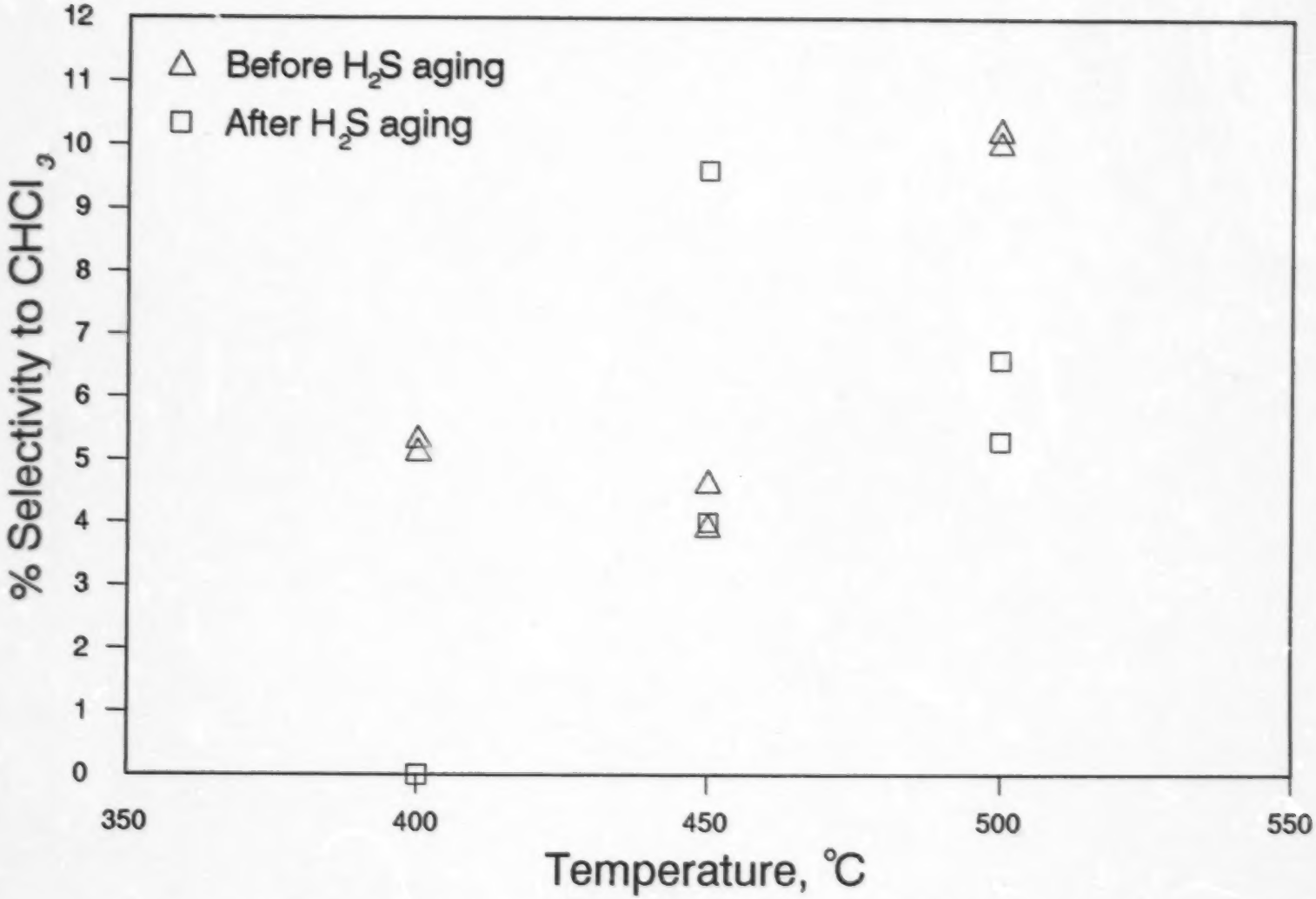

Figure 3: Selectivity to chloroform before and after H_2S poisoning

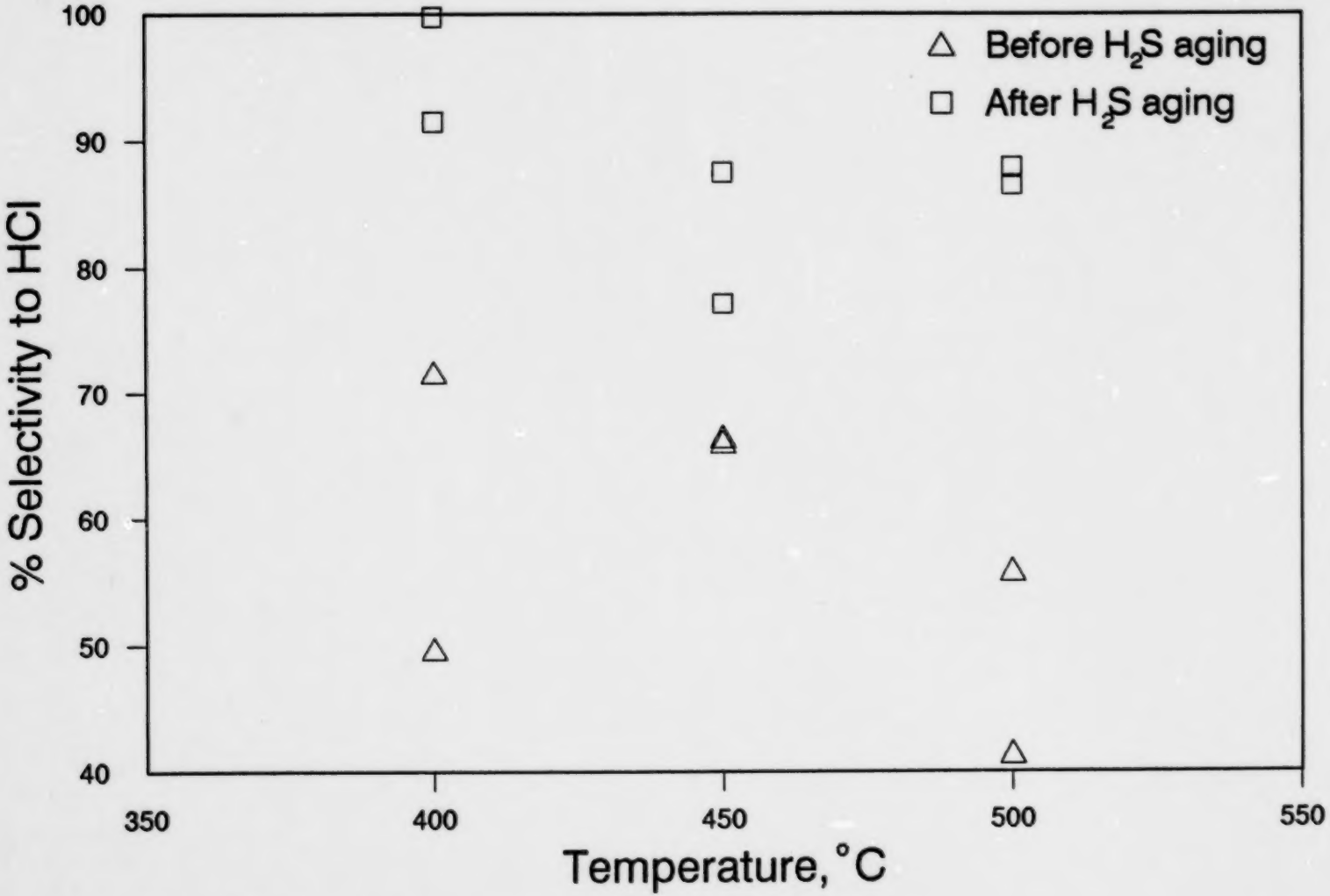

Figure 4: Selectivity to HCl before and after H_2S poisoning

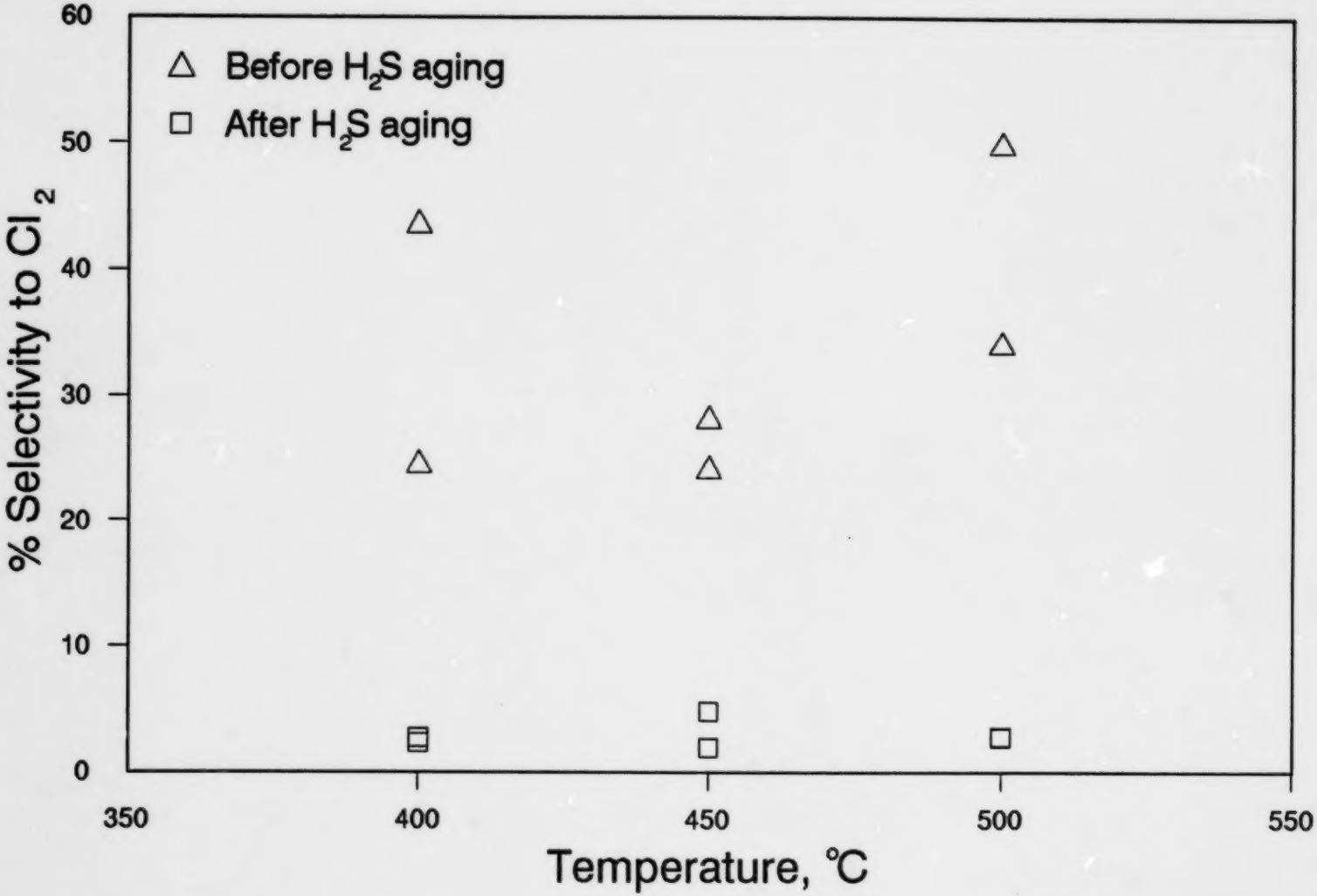

Figure 5: Selectivity to Cl_2 before and after H_2S poisoning

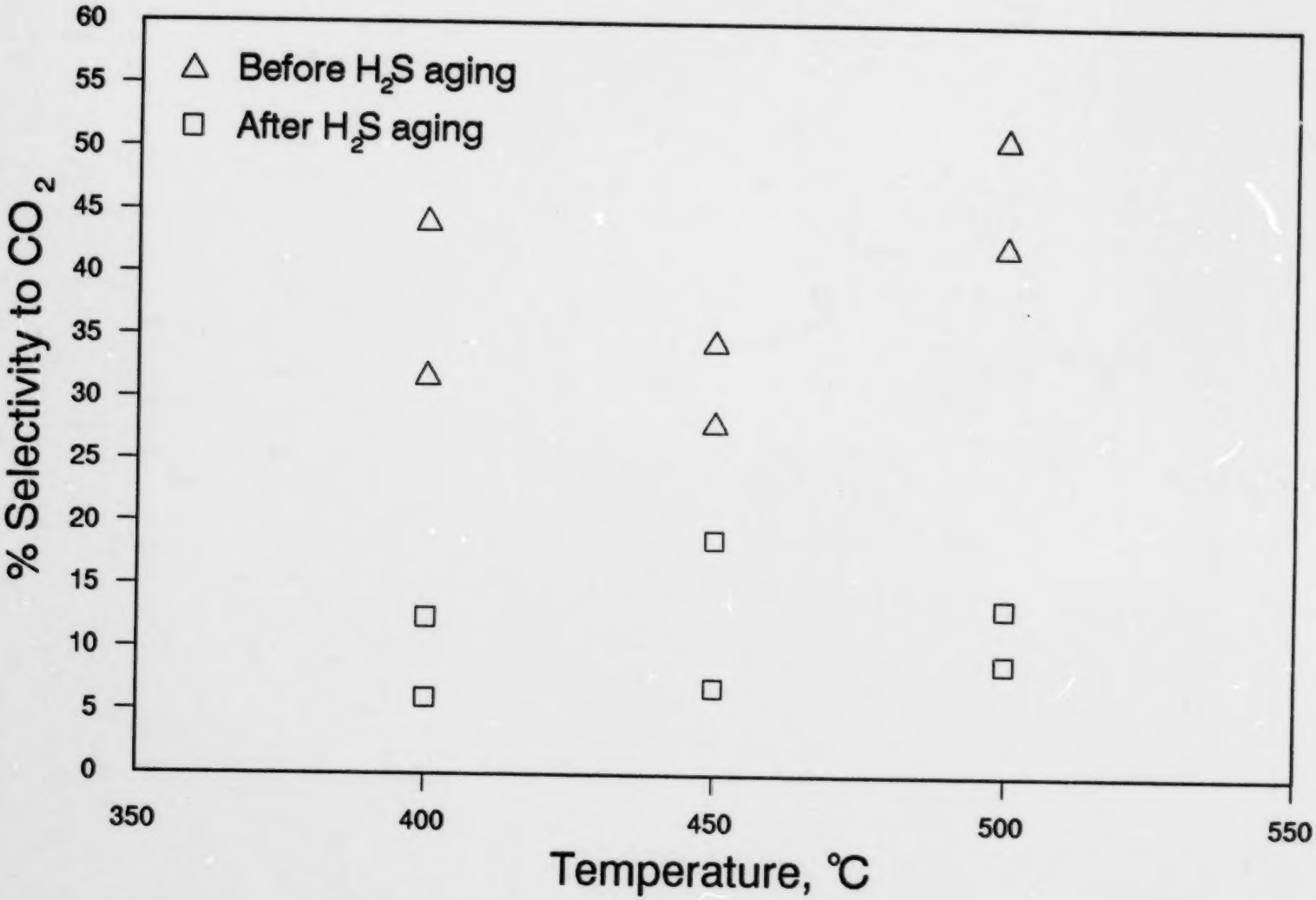

Figure 6: Selectivity to CO_2 before and after H_2S poisoning

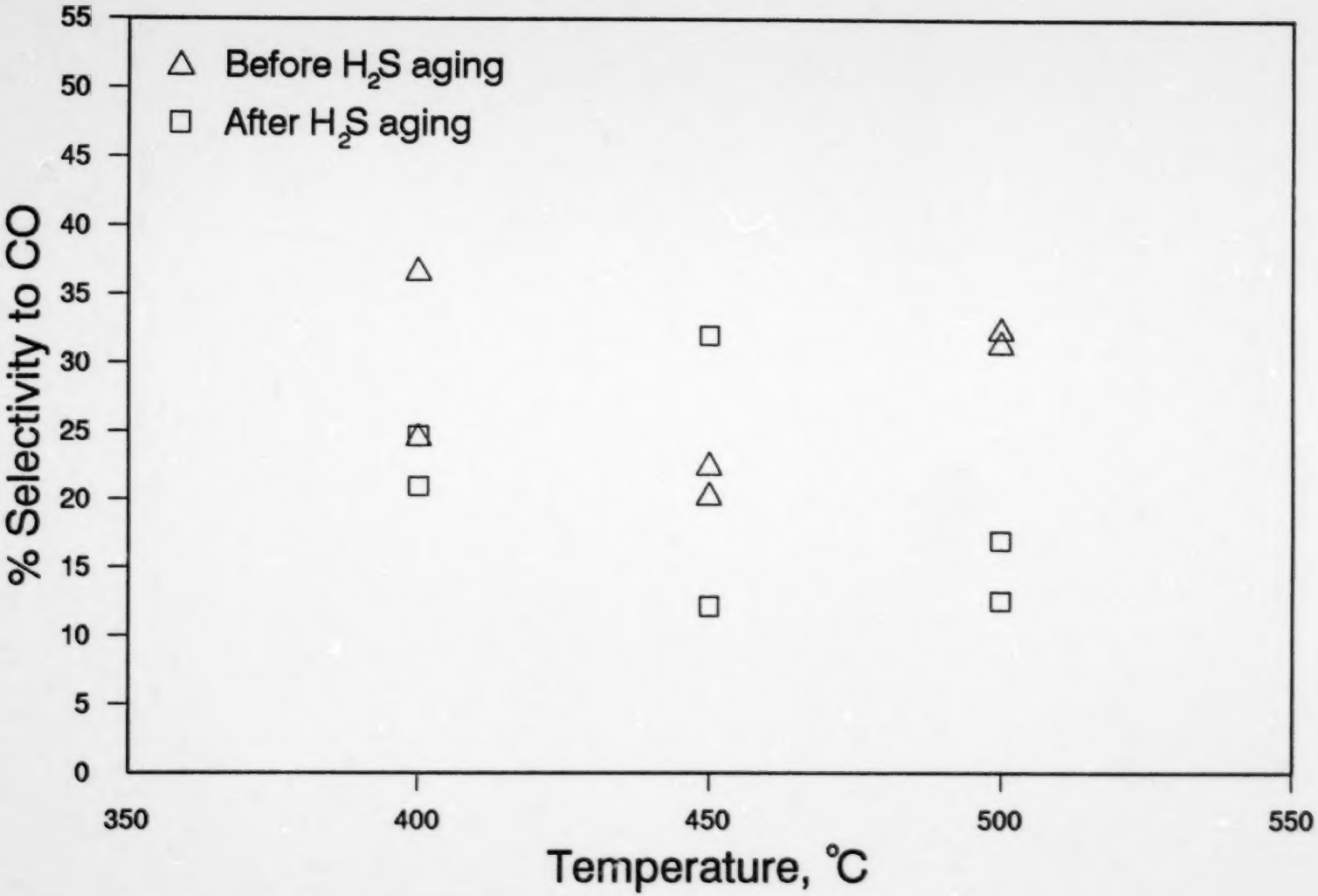

Figure 7: Selectivity to CO before and after H_2S poisoning

Table 1. Reaction Conditions and Catalyst Tube Details

Details of Experimental Conditions

Temperatures of Reaction	=	500, 450, and 400 °C
Operating Pressure	=	1 atm
Residence Time at 500 °C	=	0.31 sec
Catalyst Loading	=	1.6 wt%

Support Tube Details

Support Used	=	low surface area SiO_2 monolith
Support Surface Area	=	0.48 m^2/g
Tube Dimensions	=	1.6 cm OD, 0.6 cm ID, and 22.9 cm length
Support Composition	=	95% SiO_2, 4.1% Al_2O_3, <1% Mg, Ca, K, Na, Zr, and Hf oxides

Table 2. Compilation of Experimental Results

Temp (°C)	Feed (ppm)	Percent Conv.	Water (ppm)	Cl Balance	C Balance	C-Cl Formed/ C-Cl Broken
Catalyst: Cr_2O_3 prior to H_2S aging						
500	2179	50.0	0	99.8	90.6	0.1008
500	2533	50.4	21564	98.0	75.8	0.0274
500	1284	50.0	0	100.5	94.4	0.1011
450	3531	35.4	0	97.9	82.6	0.0394
450	2885	30.6	24477	97.5	83.2	0.0127
450	2586	34.6	0	99.6	86.1	0.0458
400	2646	23.4	0	100.2	90.4	0.0508
400	2562	17.7	25279	99.5	89.2	0.0000
400	2429	17.0	0	99.7	97.3	0.0540
Catalyst: Cr_2O_3 after H_2S aging						
500	2640	45.7	0	98.7	66.2	0.0523
500	2597	31.0	25414	102.7	76.7	0.0129
500	2702	43.7	0	98.5	71.8	0.0653
450	2272	22.5	0	103.0	85.4	0.0674
450	2184	8.7	22800	99.8	98.5	0.0000
450	1889	16.6	0	99.6	86.1	0.0458
400	1100	18.3	0	108.4	85.1	0.0000
400	1912	18.0	23299	99.2	82.8	0.0000
400	1859	12.9	0	99.2	91.4	0.0000

Table 3. Detailed Chlorine Balance

CH_2Cl_2	$CHCl_3$	HCl	Cl_2	$COCl_2$	Total
Catalyst: Cr_2O_3 prior to H_2S aging					
50.0	5.0	27.8	17.0	0.0	99.8
49.6	1.4	37.2	9.9	0.0	98.1
50.0	5.1	20.6	24.9	0.0	100.6
64.6	1.4	23.3	8.5	0.0	97.8
69.4	0.4	26.7	1.0	0.0	97.5
65.4	1.6	22.9	9.7	0.0	99.6
76.6	1.2	5.7	16.7	0.0	100.2
82.3	0.0	16.2	1.0	0.0	99.5
83.0	0.9	8.4	7.4	0.0	99.7
Catalyst: Cr_2O_3 after H_2S aging					
54.3	2.4	40.2	1.3	0.6	98.8
69.0	0.4	33.3	0.0	0.0	102.7
56.3	2.9	37.8	1.2	0.3	98.5
67.9	1.3	28.1	0.6	0.0	97.9
91.3	0.0	8.5	0.0	0.0	99.8
83.4	1.6	12.8	0.8	0.0	98.6
68.7	0.0	26.3	0.5	0.0	95.5
80.1	0.0	18.9	0.0	0.0	99.0
87.1	0.0	11.8	0.3	0.0	99.2

Table 4. Detailed Carbon Balance

CH_2Cl_2	$CHCl_3$	CO_2	CO	Total
Catalyst: Cr_2O_3 prior to H_2S aging				
50.0	3.4	21.1	16.1	90.6
49.6	0.9	17.4	7.9	75.8
50.0	3.4	25.4	15.6	94.4
64.6	0.9	9.9	7.1	82.5
69.4	0.3	10.1	3.5	83.3
65.4	1.1	11.9	7.7	86.1
76.6	0.8	7.4	5.7	90.5
82.3	0.0	4.9	2.0	89.2
83.0	0.6	7.5	6.2	97.3
Catalyst: Cr_2O_3 after H_2S aging				
54.3	1.6	4.1	5.7	65.7
69.0	0.3	3.5	3.9	76.7
56.3	1.9	5.8	7.4	71.4
67.9	0.9	2.2	3.9	74.9
91.3	0.0	2.7	4.6	98.6
83.4	1.1	3.1	5.3	92.9
68.7	0.0	1.1	4.5	74.3
80.1	0.0	0.7	0.0	80.8
87.1	0.0	1.6	2.7	91.4

Table 5. Selectivity Details

$CHCl_3$	$COCl_2$	HCl	Cl_2	CO_2	CO
Catalyst: Cr_2O_3 prior to H_2S aging					
10.0	0.0	55.6	34.0	42.2	32.2
2.7	0.0	73.8	19.6	34.5	15.7
10.2	0.0	41.2	49.8	50.8	31.2
3.9	0.0	65.8	24.0	27.9	20.1
1.3	0.0	87.3	3.3	33.0	11.4
4.6	0.0	66.2	28.0	34.4	22.3
5.1	0.0	71.4	24.4	31.6	24.4
0.0	0.0	91.5	5.6	27.7	11.3
5.3	0.0	49.4	43.5	44.0	36.5
Catalyst: Cr_2O_3 after H_2S aging					
5.3	1.3	87.9	2.8	8.9	12.5
8.7	0.0	72.9	0.0	11.3	12.6
6.6	0.7	86.5	2.7	13.3	16.9
4.0	0.0	87.5	1.9	6.9	12.1
0.0	0.0	97.7	0.0	31.0	52.9
9.6	0.0	77.1	4.8	18.7	31.9
0.0	0.0	100.0	2.7	6.0	24.6
0.0	0.0	100.0	0.0	3.9	0.0
0.0	0.0	91.5	2.3	12.4	20.9